Journal of Alloys and Compounds 673 (2016) 364–371

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Highly aligned array of $W_{18}O_{49}$/CuO core–shell nanorods and its promising NO_2 sensing properties

Yuxiang Qin*, Xiaojuan Zhang, Yang Liu, Weiwei Xie

School of Electronics and Information Engineering, Tianjin University, Tianjin, 300072, China

ARTICLE INFO

Article history:
Received 6 January 2016
Received in revised form
22 February 2016
Accepted 29 February 2016
Available online 2 March 2016

Keywords:
Tungsten oxide nanorods
Gas sensor
Core-shell nanostructures
Aligned array

ABSTRACT

Highly ordered geometrical configuration and uniform shell layer are desirable for applications of one-dimensional (1D) core–shell heterostructures in gas sensors. In this work, we put forward a novel preparation of $W_{18}O_{49}$/CuO core–shell nanorods array with high alignment and uniform shell layer through the induction of shell film sputtering to roughly aligned $W_{18}O_{49}$–core nanorods. The $W_{18}O_{49}$-core nanorods with diameter of ~20 nm were first grown via in-situ thermal oxidation of sputtered W film. Further sputtering-depositon of polycrystalline shell layer of CuO harvests a uniform $W_{18}O_{49}$/CuO core–shell nanorods array with improved alignment. Thicker shell results in better alignment. The NO_2-sensing properties of $W_{18}O_{49}$/CuO core–shell nanorods array were investigated at room temperature up to 200 °C. It is found that the formation of core–shell heterostructure lowers the optimal operating temperature of $W_{18}O_{49}$ nanorods sensor from 150 °C to near-room temperature of 50 °C. The presented heteroarray of $W_{18}O_{49}$/CuO core–shell nanorods is responsive to diluted NO_2 gas at ppb level. At 50 °C, it shows satisfactory sensing response to 0.1–1 ppm NO_2 gas with excellent dynamic response-recovery characteristics. These results are associated with the unique aligned configuration and the dual modulations of both heterojunction potential barrier at core–shell interface and the conductive carrier-accumulation channel.

1. Introduction

One-dimensional (1D) nanomaterials with large surface area, high crystallinity and low dimensionality are attractive building blocks for functional devices in nanoscale. In particular, 1D core–shell heterostructures, originating from nanowires or nanorods of binary semiconducting metal oxides, have become a focus of intensive research owing to their exciting physical/chemical properties and wide range of potential applications in advanced nanoelectronic and nanophotonic devices [1,2]. For instance, gas sensors based on core–shell oxides such as ZnO/SnO_2 nanowires [3], WO_3/ZnO nanorods [1] and VO_2/TiO_2 nanorods [4] exhibit improved selectivity and sensitivity due to the remarkable synergetic effect between both oxides; core–shell structured photoanodes have shown enhanced photo-conversion efficiency due to the highly effective charge separation at the hetero-interface [5]. Notably, the physical and chemical properties of core–shell nanostructures can be further controlled by adjusting component phases [1]. To achieve satisfying gas-sensing or photo/electrochemical properties, the ideal device topology from the theoretical and experimental studies is expected to be a perfect vertical array of 1D core–shell heterostructures [6]. Moreover, highly ordered arrays of 1D heterostructure are also much promising for use in data storage and field emission devices [7,8]. It is reported that the 1D core–shell structures could be synthesized by simple one-step route such as thermal evaporation [9] and hydrothermal method [10]) or two-step process like electrospinning followed by atomic layer deposition (ALD) [11], solution synthesis followed by photochemical reaction [12]. However up to now, all these reported 1D core–shell structures are usually either disordering in geometrical configuration or only partial shell-coating along the aligned core-array. Preparation of 1D core–shell array with high alignment and uniform shell layer on whole surface is still desirable.

In this work, we developed a novel inductive alignment process to successfully prepare uniform core–shell array of n-$W_{18}O_{49}$/p-CuO nanorods with controlled alignment. Tungsten oxide is an important wide band-gap n-type semiconductor feasible to photo/electrochromic, gas sensing, and field emission devices [13–15]. Especially, 1D nonstoichiometric $W_{18}O_{49}$ has experimentally

* Corresponding author.
E-mail address: qinyuxiang@tju.edu.cn (Y. Qin).

http://dx.doi.org/10.1016/j.jallcom.2016.02.242
0925-8388/

proved to be a promising gas-sensing material operating at near-room temperature. CuO, presenting p-type semiconductor properties, also shows interesting photo/electrochemical, gas-sensing, photovoltaic, catalytic properties [16–18]. Therefore, the presented n-$W_{18}O_{49}$/p-CuO heteroarray is expected to show exciting performances, especially due to its unique structural characteristics i.e. uniform core–shell structure and highly vertical alignment. Herein, to demonstrate the potential applications of the as-prepared aligned heterostructure, a comparative study on the gas-sensing properties of the CuO-wrapped $W_{18}O_{49}$ hetero-nanorods array and bare $W_{18}O_{49}$ nanorods are preformed. Meanwhile, the underlying gas-sensing mechanism of the heterogeneous $W_{18}O_{49}$/CuO is analysed.

2. Experimental details

2.1. Preparation and characterization of $W_{18}O_{49}$/CuO nanorods array

The core–shell array of $W_{18}O_{49}$/CuO nanorods were inductively prepared by a two-step method on the cleaned alumina substrate with a pair of interdigitated Pt electrodes in 100 nm thickness. The electrodes were deposited using RF magnetron sputtering technique. The two-step process included the direct growth of rough aligned $W_{18}O_{49}$-core nanorods on the electrode-attached substrate and subsequent sputtering-formation of CuO shell layer in company with alignment modulation. In the first step, to synthesize $W_{18}O_{49}$ nanorods, a novel route of in situ thermal oxidation of sputtering-deposited metallic W film was developed. The metallic W film with thickness of about 150–200 nm was pre-deposited on a Pt electrodes-attached alumina substrate. A physical mask was used during W-sputtering to avoid the coating of W film at the end of the electrodes. The W film-coated alumina substrate was then placed in a horizontal tube furnace. After pumped to a pressure of 10^{-3} Torr, the furnace was heated up to 650 °C in ramp of 5 °C/min and held for 1 h under argon and oxygen flow ($Ar/O_2 = 350$). Then the furnace was cooled down to room temperature. In the following step, the alumina substrate with tungsten oxide nanorods was firstly annealed at 400 °C for 1 h in air atmosphere to stabilize the crystalline and pure its surface, and then transferred to DC magnetron sputtering chamber. Copper film was sputter-deposited on whole surface of tungsten oxide nanorods in pure argon ambience. The sputtering process was performed for 1.5–3 min under a fixed sputtering power of 100 W to form continuous shell layer of Cu with different thicknesses. The formed core–shell heterostructures were further annealed at 350 °C for another 1 h in air atmosphere to obtain crystalline CuO shell layer. In this step, the alignment of $W_{18}O_{49}$-core nanorods will be modulated considerably by the film stress produced during sputtering of Cu shell. As a result, a highly aligned, uniformly coated $W_{18}O_{49}$/CuO core–shell nanorods array was obtained.

The morphology and structure of the samples were characterized with field emission scanning electron microscope (FESEM, Hitachi S4800), field emission transmission electron microscopy/energy-dispersive X-ray spectroscopy (FETEM/EDX, TECNAI G^2F-20), X-ray photoelectron spectroscopy (XPS, PERKIN ELEMER PHI-1600 ESCA), and X-ray diffraction (XRD, RIGAKU D/MAX 2500V/PC, Cu Kα radiation).

2.2. Measurement of gas-sensing properties

The gas-sensing properties of the as-prepared $W_{18}O_{49}$/CuO nanorods array were evaluated in a home-built static gas-sensing testing system consisting of a test chamber, a controllable flat heating plate, a professional digital multimeter and a data acquisition computer [19]. The top lid of the test chamber can be opened completely to assure a good recovery of the sensor during test. The sensor was placed on the heating plate fixed in test chamber. Appropriate volume of pure NO_2 gas was injected into the test chamber directly to get the desired concentration. The resistance change of the sensor during the whole measurement was continuously monitored by an UNI-T UT61E professional digital multimeter with the function of automatic measuring range adjustment. In the experiment, the tungsten oxide nanorods are found to only grow on the area deposited W film after thermal process. So during sensing test, the bare ends of Pt electrodes can be used to realize the electrically connection between the sensor and the digital multimeter. The sampling interval was set to 1 s, and the test temperature was changed from room temperature to 200 °C by adjusting the temperature controller of the heating plate. The test equipment is set in a humidity-controlled testing room, and during the measurement, the ambient relative humidity is about 30–35%.

3. Results and discussion

3.1. Microstructure characterization

The SEM images of the bare and shell layer-coated tungsten oxide nanorods on the substrate are shown in Fig. 1. Fig. 1(a) shows the cross-sectional image of the bare tungsten oxide nanorods. It can be seen that the tungsten oxide nanorods grown from the substrate exhibit a rough alignment feature. The well-defined nanorods have uniform diameter of about 20 nm, and their lengths vary from hundreds of nanometres to more than one micron. Fig. 1(b) and (c) respectively show the cross-sectional morphologies of the heteronanorods with 1.5 min- and 3 min-sputtering of copper. In comparison with the bare nanorods in Fig. 1(a), it is clearly observed that the core–shell nanorods exhibit considerable improvement in alignment. Moreover, thicker shell layer results in better alignment. The heteronanorods with 3 min-Cu sputtering are almost vertically aligned to the substrate. From Fig. 1(b) and (c), we can see that the shell layer is coated on the whole surface uniformly as evidence of the almost uniform thickness of heteronanorods along axis directions. The diameters of the core–shell nanorods with 1.5 min- and 3 min-Cu sputtering are about 30 nm and 40 nm, respectively. The corresponding top-view images in Fig. 1(d, e and f) further reveal the gradual improvement in alignment after shell sputtering-deposition.

To the best of our knowledge, similar work has never been reported by other groups. So the exact mechanism of shell layer modulation on the alignment of $W_{18}O_{49}$ nanorods array is still ambiguous. To try to explore the possible inductive mechanism of shell layer on core-nanorods array, other heteronanorods with different shell film such as V_2O_5 and TiO_2 have also been investigated in our group. Interestingly, similar improvement in alignment has also been observed. Apparently, the shell layer material has little effect on the alignment improvement for $W_{18}O_{49}$ nanorods array. It hints that the crystallographic interaction between the layers of shell and core should not be a considerable factor for the improvement of nanorods alignment. In other words, the presented process is universal for preparation of vertically aligned core–shell heteronanorods array with different shell layers. Here, we suggest that the initial geometrical posture of the quasi-aligned $W_{18}O_{49}$ nanorods, and further modulation by the film stress of shell layer occurred during sputtering should be responsible for the formation of vertically aligned and uniformly coated core–shell nanorods array [12]. Characterization on intermediate morphologies during formation of core–shell structure indicated that thermal annealing of shell layer makes the crystalline improved but shows little effect on the nanorods alignment. It suggests that the sputtering stress